

US005714550A

17 Claims, No Drawings

United States Patent 5,714,550 Patent Number: [11]Feb. 3, 1998 Shaw Date of Patent: [45] FLAME RETARDANT POLYAMODE-4,981,920 1/1991 Terashima et al. . [54] 2/1991 Taubitz et al. . 4,990,564 POLYPHENYLENE ETHER COMPOSITIONS 5,000,897 3/1991 Channibers . 3/1991 Tagaki et al. . 5,001,181 Jeremy Paul Shaw, Jankenberg, [75] Inventor: 5/1991 Abe et al. . 5,017,652 Netherlands 5/1991 Mizumo et al. . 5,017,663 5/1991 Taubitz et al. . 5,019,626 Assignee: General Electric Company, Pittsfield, [73] 6/1991 Tagaki et al. . 5,026,787 Mass. 7/1991 Avakian et al. 5,032,635 5,039,746 8/1991 Nugebauer et al... 8/1991 Brown et al.. Appl. No.: 735,484 5,041,504 5,053,458 10/1991 Taubitz et al. . Filed: Oct. 23, 1996 [22]5,055,494 10/1991 van der Meer. 5,061,746 10/1991 Gallucci et al. . Related U.S. Application Data 5,069,818 12/1991 Aycock et al. . 5,070,151 12/1991 Mizauno et al. . 5,071,894 12/1991 Weil et al. 524/492 [63] Continuation of Ser. No. 541,364, Oct. 10, 1995, abandoned. 5,073,596 12/1991 Inoue et al. . [51] 5,073,620 12/1991 Sanada et al. . C08L 77/00 1/1992 Neugebauer et al. . 5,084,523 [52] (List continued on next page.) 525/397; 524/188; 524/265; 524/405 Field of Search 525/66, 92 B, [58]FOREIGN PATENT DOCUMENTS 525/393, 397; 524/188, 265, 405 0 147 874 B1 10/1984 European Pat. Off. . 1/1985 0129825 European Pat. Off. . References Cited [56] 5/1986 European Pat. Off. . 0182163 9/1986 0 221 341 B1 European Pat. Off. . U.S. PATIENT DOCUMENTS 9/1986 0 222 129 B1 European Pat. Off. . 3,063,872 11/1962 Boldebuck. 12/1986 European Pat. Off. . 0 234 063 B1 4/1968 Finholt. 3,379,792 0-237-187-A1 2/1987 European Pat. Off. . 6/1973 Haaf. 3,737,479 0-292-153-A2 5/1988 European Pat. Off. . 6/1976 Cooper. 3,960,985 0-362-439-A1 8/1988 European Pat. Off. . 2/1982 Ueno et al. . 4,315,086 10/1989 European Pat. Off. . 0-369-169-A1 7/1982 Manuyama et al. . 4,338,421 0-381-390-A2 1/1990 European Pat. Off. . 5/1984 Lovgren et al. 0-436-136-A1 4,446,090 12/1990 European Pat. Off. . 12/1984 Lovgren et al. . 4,487,858 3/1991 0-451-563-A2 European Pat. Off. . 11/1985 Williams . 4,552,912 3/1992 0-506-386-A2 European Pat. Offf. . 4,600,741 7/1986 Aycock et al. . 5/1992 0-516-150-A1 European Pat. Off... 4,642,358 2/1987 Aycock et al. . 6/1992 European Pat. Off. . 0-523-368-A1 3/1987 Jalbert . 4,654,405 0-528-581-A1 8/1992 European Pat. Off. . 4/1987 Van der Meer. 4,659,760 0-491-187-A1 11/1992 European Pat. Off. . 3/1988 Droscher et al. . 0-549-268-A2 12/1992 4,728,693 European Pat. Off. . 4,737,938 4/1988 Grant et al. . 0-550-06-A2 12/1992 European Pat. Off. . 5/1988 Shibuya et al. . 4,743,651 0-559-485-A1 3/1993 European Pat. Off. . 4,745,157 5/1988 Yates, III et al. . 0543462-A1 5/1993 European Pat. Off. . 6/1988 Van der Meer. 4,749,737 2/1992 Japan . 4-39354 4,755,566 7/1988 Yates, III et al. . 3/1992 4-88058 Japan . 7/1988 Droescher et al. . 4,760,115 7/1992 4-198354 Japan . 4,772,664 9/1988 Ueda, et al. . 4-202256 7/1992 Japan . 4,792,586 12/1988 Ham. 3/1993 070681 Japan 524/405 1/1989 Grant et al. . 4,798,865 2035337 6/1980 United Kingdom. 4/1989 Wroczynski . 4,822,836 8/1988 WIPO . WO 88/06167 WO 93/13251 4/1989 vam der Meer. 4,822,837 WIPO. 7/1993 4/1989 Aycock et al. . 4,824,915 OTHER PUBLICATIONS 4,826,933 5/1989 Grant et al. . 6/1989 Mawatari et al. . 4,839,425 207152K, May 1975, Chemical Abstracts CS-A-157841 8/1989 van der Meer. 4,857,575 8/1989 Yates, III et al. . 4,859,739 Primary Examiner---David Buttmer 4,866,114 9/1989 Taubitz et al. . 4,866,144 9/1989 Best et al. . ABSTRACT [57] 4,871,795 10/1989 Pawar ... 4,873,286 10/1989 Galllucci et al. . The invention is directed to a polymer composition com-4,874,810 10/1989 Lee, Jr. et al. . prising: 4,877,847 10/1989 Masu et al. . a) a blend comprising at least one polyamide and at least 4,885,334 12/1989 Mayumi et al. . one polyphenylene ether: 4,888,397 12/1989 Van der Meer et al. . b) at least one polymeric siloxane compound; and 4,889,889 12/1989 Yates, III. 4,923,924 5/1990 Grant. c) at least one boron compound. 4,929,675 5/1990 Abe et al. .

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FLAME RETARDANT POLYAMIDE. POLYPHENYLENE ETHER COMPOSITIONS

This is a continuation of application Ser. No. 08/541,364 filed on Oct. 10, 1995 now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to novel polyamide-polyphenylene $_{10}$ ether compositions.

Polymer blends which contain polyamide and polyphenylene ethers (PPE) constitute an invaluable class of engineering thermoplastic resins. Resins of polyphenylene ethers are characterized by a unique combination of chemical, 15 physical and electrical properties. For instance, they are resistant to many solvents and generally display high impact strengths. As a result of this unique combination of properties, resins of polyphenylene ethers are suitable for a broad range of commercial applications.

Efforts have been made to prepare polymer blends which, while retaining their characteristic hydrolyric stability, dimensional stability and dielectric properties, have higher heat deflection temperatures. Particularly, there is a demand for immiscible blends, like polyamide blends, which possess increased heat deflection properties since they are, for instance, conventionally used in parts exposed to high temperatures in the automotive industry.

While thermoplastic resins and blends possess the above-described advantageous properties, they, like many other organic polymeric materials, are particularly desired when they possess flame retardant properties.

It is of increasing interest to prepare thermoplastic resins and blends prepared therefrom that are fire resistant. Such preparation conventionally employs adding flame retardant additives to the polymer/blend. However, blends comprising said flame retardant additives are invariably environmentally unfriendly.

In addition thereto, the inclusion of fire retardant additives 40 usually unfluences the mechanical properties (impact resistance; heat resistance) negatively.

The instant invention, therefore, is directed to novel polymer compositions that display superior flame retardant properties.

2. Description of the Related Art

Efforts have been made to prepare polyamide-PPE compositions that possess flame retardant properties. In U.S. Pat. No. 4,866,144, self-extinguishing theroplastic polyphenylene ether/polyamide molding materials are disclosed. Said materials comprise triazine compounds such as cyanuric acid, cyanuric acid derivatives and mixtures thereof and preferably melamine and/or melamine cyanurate as flame proofing agents.

Other investigators have focused their attention on polyamide blends in order to improve flame retardancy. European Patents 0436136 and 0129825 describe blends of polyphenylene ethers and polyamides comprising phosphorus containing compounds in order to enhance flame retardant properties.

Still others, such as those described in European Patent 0369169, have revealed polymer compositions comprising polysiloxanes, polyamides and polyphenylene ethers having flame retardant properties.

The instant invention is based on the observations that polyamide-PPE compositions comprising boron compounds

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and polysiloxane compounds unexpectedly display flame retardant properties and good heat resistances. Moreover, the instant polyamide-PPE compositions do not contain halogens and red phosphorous.

SUMMARY OF THE INVENTION

Accordingly the invention is directed to novel polyamide-PPE compositions that unexpectedly display flame retardant properties and improved heat resistances, said composition comprising:

- a) a blend comprising at least one polyamide and at least one polyphenylene ether;
- b) at least one polymeric siloxane compound; and
- c) at least one boron compound.

In the instant invention, flame retardant properties mean that UL-94 is v-0 or V-1 at 1.6 mm and improved heat resistance mean a Vicat of greater than about 200° C., wherein the Vicat temperature the softening temperature at which a plastic starts to soften as specified according to ISO 306.

The present invention is based on the surprising discovery, that the use of a polymeric siloxane compound, preferably polysiloxane, in combination with boron compounds provides an improved flame retardant action in polyamide-polyphenylene ether blends. More in particular it is important that the negative influence of those compounds on the mechanical properties, such as impact resistance (IZOD) and heat resistance (Vicat) is relatively low, especially in comparison to the other environmentally friendly flame retardant additives.

DETAILED DESCRIPTION OF THE INVENTION

According to the present invention the polymer composition comprises as main components the PA-PPE blend, polysiloxane, at least one boron compound, and as optional components inorganic phosphate and titanium oxide. The use of organic based phosphorous compounds (such as organic phosphate and phosphine oxides) is not precluded in relation to the present invention, however, in view of their negative influence on the Vicat temperature they are not recommended.

The polyphenylene ethers employed in the instant invention are typically prepared by the oxidative coupling of at least one monohydroxyaromatic compound such as 2,6-xylenol or 2,3,6-trimethylphenol. Catalyst systems are generally employed for such coupling; they typically contain at least one heavy metal compound such as a copper, manganese or cobalt compound, usually in combination with various other materials.

Furthermore, polyphenylene ethers suitable for use in the practice of the present invention may be prepared by any of a number of processes ulilizing precursor corresponding phenols or derivatives thereof. Examples for their production are disclosed in U.S. Pat. Nos. 3,306,874; 3,306,875; 3,257,357; 3,257,358; 3,337,501; and 3,787,361, all incorporated herein by reference.

Additional useful polyphenylene ethers are those which comprise molecules having at least one aminoalkyl-containing end group. The aminoalkyl radical is typically located in an ortho position to the hydroxygroup. Products containing such end groups may be obtained by incorporating an appropriate primary or secondary monoamine such as di-n-butylamine or dimethylamine as one of the constituents of the oxidative coupling reaction mixture. Also frequently

present are 4-hydroxybiphenyl end groups, typically obtained from reaction mixtures in which a by-product diphenoquinone is present, especially in a copper-halidesecondary or tertiary arnine system. A proportion of the polymer molecules may contain at least one of said 5 aminoalkyl-containing and 4-hydroxybiphenyl end groups.

The polyamides employed in the instant invention are obtained, for instance, by polymerizing a monoaminemonocarboxylic acid; or a lactam thereof having at least 2 carbon atoms between the amino and carboxylic acid group or by 10 polymerizing substantially equimolar proportions of a diamine which contains at least 2 carbon atom amino groups and a dicarboxylic acid; or by polymerizing a monoamino carboxylic acid or a lactam thereof as defined hereinabove together with substantially equimolar proportions of a 15 diamine and a dicarboxylic acid. The dicarboxylic acid in the form of a functional derivative thereof; for example, an ester or acid chiloride.

The term "substantially equimolecular" proportions (of the diamine and of the dicarboxylic acid) is used to cover both strict equimolecular proportions and slight departures therefrom which are involved in conventional techniques for stabilizing the viscosity of the resultant polyamides.

Examples of the aforementioned monoaminomorocarboxylic acids or lactams thereof which are useful in preparing the polyamides include those compounds containing from 2 to 16 carbon atoms between the amino and carboxylic acid groups, said carbon atoms forming a ring with the ----CO---NH-group in the case of a lactam. As particular examples of aminocarboxylic acids and lactams there may be mentioned aminocaproic acid, butyrolactam, pivalolactam, caprolactam, capryl-lactam, enantholactam, undecanolactam, dodecanolactam and 3- and 4-aminobenzoic acids.

Diamines suitable for use in the preparation of the polyamides include straight chain and branched, alkyl, aryl and alkyl-aryl diamines. Such diamines include, for example, those represented by the general formula I

$$H_2N(CH_2)_nNH_2$$

wherein n is an integer of from 2 to 16, such as trimethylene diamine, tetramethylene diamine, pentamethylene diamine, octamethylene diamine and especially hexamethylene diamine, as well as trimethyl hexamethylene diamine, metaphenylene diamine, meta-xylene diamine and the like.

The dicarboxylic acids may be aromatic, for example, isophthalic and terephthalic acids. Preferred dicarboxylic acids are of the formula II

wherein Y represents a divalent aliphatic group containing at least 2 carbon atoms, and examples of such acids are sebacic pirnelic acid and adipic acid.

Typical examples of polyamides (Nylons) useful in the instant polyamide compositions include for example polyamides 4/6, 6, 6/6, 11, 12, 6/3, 6/4, 6/10 and 6, 12 as well as polyamides resulting from terephthalic acid and/or isoph- 60 thalic acid and trimethyl hexamethylene diamine, polyamides resulting from adipic acid and meta xylylene diamines, polyamides resulting from adipic acid, azelaic acid and 2,2-bis-p-aminocyclohexyl)propane, semicrystalline polyamides resulting from combinations of 65 terephthalic and/or isophthalic and/or adipic acids with hexamethylene diamine, semi-crystalline polyamides result-

ing from terephthalic and/or isophthalic acids and hexamethylene and 2-methyl pentamethylene diamines, and polyamides resulting from terephthalic acid and 4,4'-diaminodicyclohexylmethane. Mixtures and/or copolymers of two or more of the foregoing polyamides or prepolymers, respectively, are also within the scope of the present invention. Preferred polyamides are the polyamides 6, 6/6, 6/10 and 4/6, most preferably polyamide 6/6.

It is also understood that use of the term "polyamides" herein and in the appended claims is intended to include the toughened or super tough polyamides. Super tough polyamides or super tough nylons, as they are more commonly known, are available commercially, e.g., from E. I. dupont under the tradename Zytel ST, or may be prepared in accordance with a number of U.S. patents, including, among others, Epstein, U.S. Pat. No. 4,174,358; Novak U.S. Pat. No. 4,474,927; Roura, U.S. Pat. No. 4,346,194; and Joffrion, U.S. Pat. No. 4,251,644, herein incorporated by reference. These super tough nylons are prepared by blending one or more polyamides with one or more polymeric or copolymeric elastomeric toughening agents. Suitable toughening agents are disclosed in the above-identified U.S. patents, as well as in Caywood, Jr., U.S. Pat. No. 3,884.882 and Swiger, U.S. Pat. No. 4,147,740 and Gallucci et al., "Preparation and Reactions of Epoxy-Modified Polyethylene", J. Appl. Poly., Sci., Vol. 27, pp. 425-437 (1982) herein incorporated by reference. Typically, these elastomeric polymers and copolymers may be straight chain or branched as well as graft polymers and copolymers, including core-shell graft copolymers, and are characterized as having incorporated therein either by copolymerization or by grafting on the performed polymer, a monomer having functional and/or active or highly polar groupings capable of interacting with or adhering to the polyamide matrix so as to enhance the toughness of the polyamide polymer.

While it is preferred that the polyamide compositions of the instant invention comprise blend of polyamides and polyphenylene ethers, it is also within the scope of this invention to include in said compositions acrylic polymers including polymethylmethacrylate, acrylonitrile styrene 40 copolymers, styrene-acrylonitrile-butadiene copolymers, polyvinyl chloride, polystyrene, butyrates, polyaliphatics, polycarbonates and polyesters, cellulosic, phenolic, amino and epoxy resins.

It is also within the scope of the instant invention to 45 employ compatibilization agents in the blends. Such compatibilization agents include, for instance, compounds selected from the group consisting of tetracarboxylic acids of aromatic and aliphatic compounds, alicyclic compounds, dianhydride derivatives and halogen substituted phthalic 50 anhydrides. A more detailed description of blend compatibilization may be found in U.S. Pat. No. 4,826,933, the disclosure of which is incorporated herein by reference.

The blending ratio of polyamide to polyphenylene ether units is about 5 to about 95% by weight, preferably about 10 acid, octadecanedoic acid, suberic acid, glutaric acid, 55 to about 70% by weight of polyphenylene ether to about 90 to about 30% by weight of polyamide.

Impact modifiers for polyphenylene ether-polyamide blends are well known in the art. They are typically derived from one or more monomers selected from the group consisting of olefins, vinyl aromatic monomers, acrylic and alkylacrylic acids and their ester derivatives as well as conjugated dienes. Especially preferred impact modifiers are the rubbery high-molecular weight materials including natural and synthetic polymeric materials showing elasticity at room temperature. They include both homopolymers and copolymers, including random, block, radial block, graft and core-shell copolymers as well as combinations thereof.

A particularly useful class of impact modifiers comprises the AB (diblock) and ABA (triblock) copolymers and coreshell graft copolymers of alkenylaromatic and diene compounds, especially those comprising styrene and butadiene or isoprene blocks. The conjugated diene blocks may 5 be partially or entirely hydrogenated, whereupon they may be represented as ethylene-propylene blocks or the like and have properties similar to those of olefin block copolymers. Examples of triblock copolymers of this type are polystyrene-polybutadiene-polystyrene (SBS), hydroge- 10 nated polystyrene-polybutadiene-polystyrene (SEBS), polystyrene-polyisoprene-polystyrene (SIS), poly(amethylstyrene)-polybutadiene-poly(a-methylstyrene) and poly(a-methylstyrene)-polyisoprene-poly(a-methylstyrene). Particularly preferred triblock copolymers are available 15 commercially as CARIFLEX®, KRATON D® and KRA-TON G® from Shell.

Also suitable as impact modifiers are the ionomer resins, which may be wholly or partially neutralized with metal ions, and the core-shell type graft copolymers. In general, 20 the latter have a predominantly conjugated diene or crosslinked acrylate rubbery core and one or more shells polymerized thereon and derived from monoalkenylaromatic and/or acrylic monomers alone or in combination with other vinyl monomers. Included are copolymers wherein an 25 interpenetrating network of the resins employed characterizes the interface between the core and shell, such as those available from General Electric Company and described in U.S. Pat. No. 3,944,631.

Other impact modifiers include the above-described types 30 containing units having polar groups or active functional groups, as well as miscellaneous polymers such as Thiokol rubber, polysulfide rubber, polyurethane rubber polyether rubber (e.g., polypropylene oxide), epichlorohydrin rubber, ethylene-propylene rubber, thermoplastic polyester elas- 35 tomers and thermoplastic ether-ester elastomers.

Additionally, the polyamide and polyphenylene ether blends may further comprise, for instance, functionalized polyphenylene ethers, polycarboxylic acids, ester groups, epoxy groups, anhydride groups, rubbers or any other comventional moiety employed to improve the properties of the blend.

The polymeric siloxane compound used in the present invention may be selected from the group of polysiloxane and siloxane copolymers, such as polyphenylene ether or 45 polyetherimide siloxane copolymers. The preferred polysiloxane compounds employed in the instant invention are commercially available and are represented by the formula IV

aminoalkyl)-3-aminoalkyl group, provided that \mathbb{R}^2 is a \mathbb{C}_{1-5} alkyl group when w is 1 and a N-(2-aminoalkyl)-3-aminoalkyl group when w is 0. It is often preferred that \mathbb{R}^2 is a methyl group or a N-(2-aminoethyl)-3-aminopropyl group. \mathbb{R}^3 is hydrogen or a \mathbb{C}_{1-5} alkyl group, preferably a methyl group. W is 0 or 1 and x and y are each independently an integer from 1 to 7 and z is an integer from 0 to 7. It is noted herein that any combination of compounds represented by formula IV may be employed.

It is also within the scope of the invention to employ polysiloxanes represented by the formulae V and VI

$$Z_1 - X_1 - O - \begin{cases} V^1 & V^5 & V^5 \\ 1 & 1 \\ Si - O - Si - Si - X_2 - Z_2 \\ V^2 & V^4 & V^6 \end{cases}$$

and

wherein m+n has a value of 5-2000, V¹-V¹⁵, each independently of each other, represent a hydrogen atom or one of the following groups having 1-12 carbon atoms: alkyl, alkoxy, alkenyl, aryl, aralkyl, alkylaryl, which groups may be halogenated; wherein X_1, X_2, X_3 , each independently of each other, represent one of the following groups; alkylene, cycloalkylene, arylene, aralkylene, alkylarylene; wherein Z_1 , Z_2 , Z_3 each represent one of the following groups: $--NV^{16}V^{17}$, $--NH--(CH₂)₆---NV^{16}V^{17}$ in which V^{16} and V¹⁷, each independently of each other, represent a hydrogen atom or an alkyl group having 1-12 carbon atoms, q has a value from 1-10, an aliphatic or cycloaliphatic epoxide, a carboxylic acid or anhydride group, \mathbb{Z}_1 or \mathbb{Z}_2 is a hydrogen atom, in which, however, the compound of formula V may not comprise simultaneously an amine group and an epoxide group or not simultaneously an amino group and a carboxylic acid group, or not simultaneously an epoxide group, and a carboxylic acid or anhydride group.

One of the important components of the present invention is the boron compound. Within the scope of the present invention organic and inorganic boron compounds may be used, the amount of the compounds being such that the boron content of the polymer composition, calculated as atomic boron, is between 0.02 and 5, preferably between 0.2 and 1 wt. %.

$$\begin{array}{c|c}
R^1 & R^2 & IV \\
R^1 & Si & Si \\
Si & Si \\
Si & Si \\
R^1 & Si & R^1
\end{array}$$

$$\begin{array}{c|c}
R^1 & R^1 & R^1 \\
R^1 & Si & R^1
\end{array}$$

$$\begin{array}{c|c}
R^1 & R^1 & R^2 & R^3 \\
R^1 & Si & R^1
\end{array}$$

wherein each \mathbb{R}^1 is independently a \mathbb{C}_{1-5} alkyl group and 65 preferably a methyl group and \mathbb{R}^2 is a \mathbb{C}_{1-5} alkyl group or a primary or secondary amino group such as a N-(2-

Suitable boron compounds are i.a. boric acid, metal borates, boron phosphate, perborates and the like. More in particular preferred are metal borates (and perborates), such

alkali metal borate (sodium, potassium etc), alkaline earth borates (calcium, barium and magnesium) and transition metal borates, such as zinc borate. Those metal borates, but also the metal perborates, are preferably used in the anhydrous form.

According to the invention the composition additionally may contain inorganic phosphates and/or titanium oxide. Examples of suitable inorganic phosphates are the alkali metal (including ammonium) phosphates, alkali metal hydrogen phosphates, alkali metal pyrophospates and the like. In a specifically preferred embodiment the boron compound and the inorganic phosphate may be combined in boron phosphate, which gives a clearly improved flame retardant action. Also the use of titanium oxide improves the properties of the polymer composition.

As the use of calcium sulphate has been found to improve the comparative tracking index, the use thereof in the compositions of the invention, preferably in amounts between 5 and 20 wt. % of the composition is preferred.

The amounts of both the phosphate compound and the 20 titanium oxide may be selected within wide ranges, each being preferably between 0.1 and 20wt. % of the total of the polymer composition.

It is also noted herein that the polyamide compositions of this invention may also contain conventional ingredients such as fillers, additional flame retardants (such as tripiperidine phosphine oxide and magnesium or aluminum hydroxide), pigments, dyes, stabilizers, anti-static agents, crystallization aids, mold release agents and the like, as well as resinous components not previously discussed.

Other additives that may be employed to enhance flame retardancy in the instant invention include phosphine oxides, such as triarylphosphine oxides and aromatic phosphates, especially diphosphates. Illustrative examples of triarylphosphine oxides include triphenylphosphine oxide, triarylphosphine oxide, trinonylphosphine oxide and trinaphtylphosphine oxide. Triphenylphosphine oxide is often preferred. The aromatic diphosphates that may be employed in this invention have the formula VII

wherein each A and A¹ are independently a substituted or unsubstituted aliphatic, alicyclic or aromatic radical 45 and Q is a covalent bond linking a carbon in each A or a bridging radical selected from the group consisting of CH₂, C(CH₃)₂, S, SO₂, CO,O and N==N and t is an

integer from 0 to 4. A suitable example of an aromatic monophosphate is triphenylphosphate.

Additional additives that may be employed in the instant invention to enhance flame retardancy include melamine cyanurate and aluminium and magnesium hydroxide. Fillers such as mineral fillers may be added, such as calcium or barium sulphate.

The method for producing the blends employed in the present invention is not particularly limited, and the conventional methods are satisfactorily employed. Generally, however, melt blending methods are desirable. The time and temperature required for melt-blending are not particularly limited, and they can properly be determined according to the composition of the material. The temperature varies somewhat with the blending ratio of the polyphenylene ether to polyamide, but it is generally within a range of 270° to 350° C. A prolonged time and/or a high shear rate is desirable for mixing, but the deterioration of the resin composition advances. Consequently, the time needs to be determined taking into account these points.

Any of the melt-blending methods may be used, if it can handle a molten viscous mass. The method may be applied in either a batchwise form or a continuous form. Specifically, extruders, Banbury mixers, rollers, kneaders and the like may be employed.

The following examples illustrate the production and properties of the flame retardant polyamide/polyphenylene ether compositions of the instant invention.

Examples

A number of blends were prepared by tumble mixing a precompounded blend of polyphenylene ether and polyamide (PA) 66, with various additives, followed by extrusion at 290° C. and granulation. The granules were heated to 300° C. and molded into 1.6 mm UL test bars.

The silicone oil used in the examples consists of a blend of four polymers corresponding to formula IV in the description (2 parts: w=0; x, y, z=5; R¹=methyl, R²=N-2-(aminoethyl)-3-aminopropyl; R³=methyl, 3 parts: w=0; x, y, z=5; R¹, R²=methyl; R³=methyl, 2 parts: w=0; z=0; x=5, y=5; R¹, R²=methyl; R³=H; 1 part: w=1; x, y, z=5; R¹, R²=methyl; R³=methyl)

Examples 14 and 15 are based on precompounded PA-6 blends. Examples 16 and 17 were prepared from a precompounded PPE/PA blend, and separately added PA.

In the following tables the composition (in parts by weight) and the properties of the blends have been compiled.

Composition	1	2	3	4	5	6	7	8	9	10
PPE/PA (50/50)	1:00	95	98	93	89.5	89.5	89.5	89.5	89.5	89.5
Silicone oil			2	2	2	2	:2:	2	2	2
Zinc borate					8.5	3	3	3	3	3
(anhydrous)										
Boron phosphate		.5		5				· =		
Aluminium metaphosphate						8.5			14881	
Calcium pyrophosphate				,			5.5		· -	
Trilithium phosphate		·					=	5.5		
Magnesium metaphosphate							=		5.5	, , -
Zinc pyrophosphate										5.5
Vicat °C.	2.22	221	217	218	216	218	219	217	219	219
UL-class	ЖB	HB	HIB	\mathbf{v}_0	$\mathbf{V}1$	VO	V1	\mathbf{V}_1	V 1	V1
An home of grant an	(drip)	(drip)	(drip)							
Izod/notched (kJ/m²)	5.5	4.2	7.5	6.4	6.7	6.0	5.3	6.9	5.8	5.3

-continued

	Example								
Composition	11	12	13	14*	15*	16	17		
PIPIEMIEM (60V4O)	93					٠			
PIPIEMPA (SOVSO)		84.49	86.49	78	73	32	32		
PLAL						51	41		
Sillicone oil	2	2		2	2	2	2		
Borom phosphate	5			5	5	10	1.0		
Aluminium metaphosphate		5.5	5.5						
Zinc borate		3	3		·				
LiO ₂		5	5		5	5	:5		
Carbon black		0.01	0.01		44	******			
Calcium sulfate	****			1.5	15	,	10		
Vicat °C.	213			204	205	212	230		
UL-class	V 1	VO	HB	V:2	\mathbf{V}_{1}	$\mathbf{V}2$	V2		
izod /motched k:I/ma ²)	4.9	4.2	4.3	3.7	3.3	2.8	2		
CLI (V)				450	550	350	450		

*: PA 6 based

I claim:

- 1. A composition comprising:
- a) a blend comprising at least one polyamide and at least one polyphemylene ether;
- b) at least one polymeric siloxane compound represented by the formula:

wherein each \mathbb{R}^1 is independently a \mathbb{C}_{1-5} alkyl group, \mathbb{R}^2 is a \mathbb{C}_{1-5} alkyl group or a primary or secondary amino group, 45 provided that \mathbb{R}^2 is a \mathbb{C}_{1-5} alkyl group when w is 1 and a N-(2-aminoalkyl)-3-aminoalkyl group when w is 0, \mathbb{R}^3 is hydrogen or a \mathbb{C}_{1-5} alkyl group, w is 0 or 1 and x and y are each independently an integer from 1 to 7 and z is an integer from 0 to 7; and

- c) at least one boron compound.
- 2. The polymer composition according to claim 1, wherein the boron compound is selected from the group 55 consisting of metal borates, boric acid, organic boron compounds, perborates, boron phosphate and mixtures of two or more of these boron compounds.
- 3. The polymer composition according to claim 2, wherein the boron compound is zinc borate, boron for phosphate, or mixtures of zinc borate and boron phosphate.
- 4. The polymer composition according to claim 1, wherein additionally at least one inorganic phosphate compound d) is present.
- 5. The polymer composition according to claim 1, wherein the amount of polyphenylene ether in the

polyamide-polyphenylene ether blend is not more than 95 wt. %.

- 6. The polymer composition according to claim 5, wherein the amount of polyphenylene ether in the polyamide-polyphenylene ether blend is between 10 and 70 wt. %.
- 7. The polymer composition according to claim 5, wherein the amount of polymeric siloxane compound is between 0.1 and 20.
- 8. The polymer composition according to claim 7, wherein the amount of boron compound, calculated as atomic boron, is between 0.02 and 5 wt. %.
 - 9. The polymer composition according to claim 7, wherein the amount of polymeric siloxane compound is between 1 and 5 wt. % of the composition.
 - 10. The polymer composition according to claim 1, wherein the composition additionally contains as component e) titanium oxide, or as component f) calcium sulphate or a combination of both.
 - 11. The polymer composition of claim 1 wherein the amounts of components (a), (b), and (c) are sufficient to provide a composition with a UL-94 V-2 rating or better at 1.6 mm.
 - 12. The polymer composition of claim 1 wherein the amounts of components (a), (b), and (c) are sufficient to provide a composition with a UL-94 V-1 rating or better at 1.6 mm.
 - 13. The polymer composition of claim 1 wherein the amounts of components (a), (b), and (c) are sufficient to provide a composition with a UL-94 V-0 rating at 1.6 mm.
 - 14. The polymer composition of claim 1 further comprising compatibilization agents.
 - 15. The polymer composition of claim 14 further comprising impact modifiers.
 - 16. A composition consisting essentially of:

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- a) a blend consisting essentially of at least one polyamide and at least one polyphenylene ether;
- b) at least one polymeric siloxane compound represented by the formula:

$$\begin{array}{c|c}
R^{2} & R^{1} \\
Si & R^{2} \\
R^{1} & Si \\
R^{1} & Si
\end{array}$$

$$\begin{array}{c|c}
R^{1} \\
Si & O
\end{array}$$

$$\begin{array}{c|c}
R^{1} \\
O & R^{1}
\end{array}$$

wherein each \mathbb{R}^1 is independently a \mathbb{C}_{1-5} alkyl group, \mathbb{R}^2 is a \mathbb{C}_{1-5} alkyl group or a primary or secondary amino group, provided that \mathbb{R}^2 is a \mathbb{C}_{1-5} alkyl group when w is 1 and a N-(2-aminoalkyl)-3-aminoalkyl group when w is 0, \mathbb{R}^3 is hydrogen or a \mathbb{C}_{1-5} alkyl group, w is 0 or 1 and x and y are each independently an integer from 1 to 7 and z is an integer from 0 to 7; and

c) at least one boron compound.

17. The polymer composition of claim 16 additionally consisting essentially of at least one member of the group consisting of an inorganic phosphate compound; titanium oxide; calcium sulfate; and a combination of titanium oxide and calcium sulfate.

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